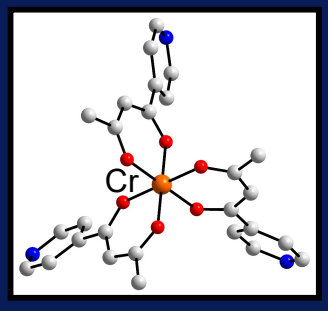
Competing supramolecular interactions in crystals of heavy-element compounds – a consideration of the energies of association between molecules

Edward R.T. Tiekink

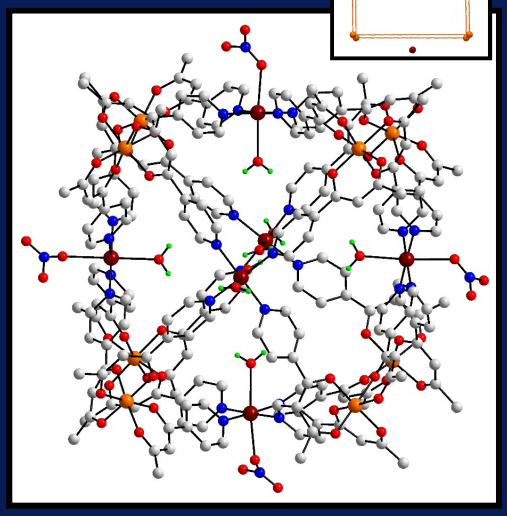
Research Centre for Crystalline Materials

2nd Southeast Asian Conference on Crystal Engineering (SEACCE-2):
August 6-8th, 2018

Molecular magnets

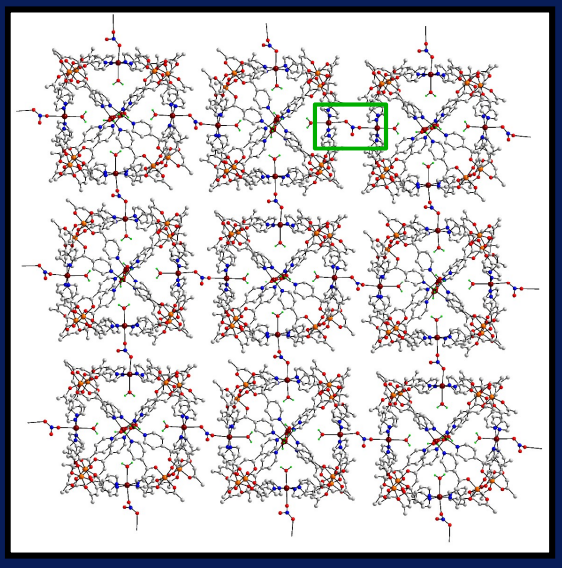


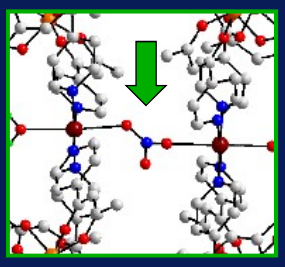
+ $Cu(NO_3)_2$



Sanz *et al.*, *Angew. Chem., Int. Ed.* **54** (2015) 6761.

Molecular magnets



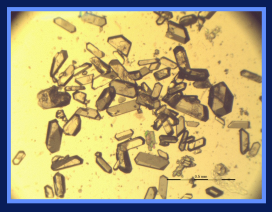


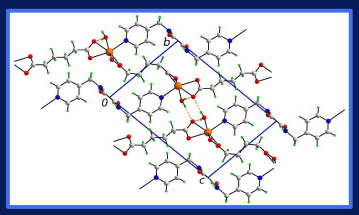
Sanz *et al.*, *Angew. Chem., Int. Ed.* **54** (2015) 6761.

Crystals?

Why do crystals form?

How do crystals form?



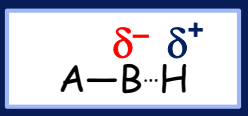


Molecular packing

Well known…

Hydrogen-bonding (HB)
Halogen-bonding (HB)

$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

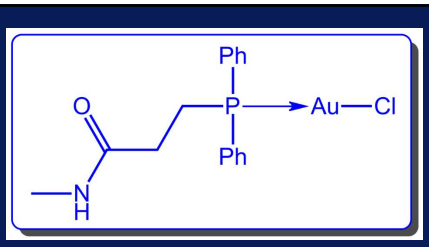


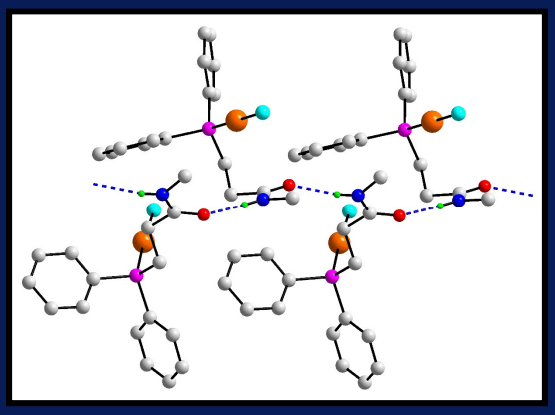
Molecular packing

$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

~~Do not always form~~

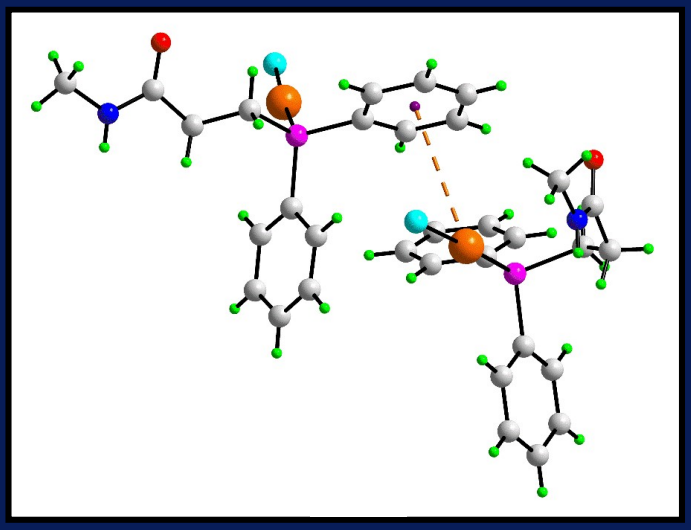
May not extend in 3-D





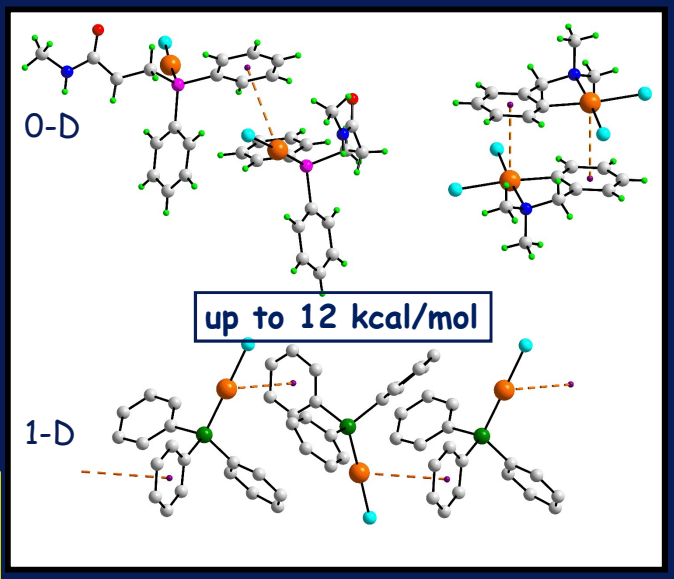
Schmidbaur *et al*., *Inorg. Chem*. **35** (1996) 637; Coord. Chem. Rev. **275** (2014) 130.

Intermolecular Au···π(arene) interactions



CrystEngComm **11** (2009) 1176; *Gold Bull*. **46** (2013) 81.

Intermolecular Au···π(arene) interactions



RSC Advances **5** (2015) 41401.

Gold Chemistry

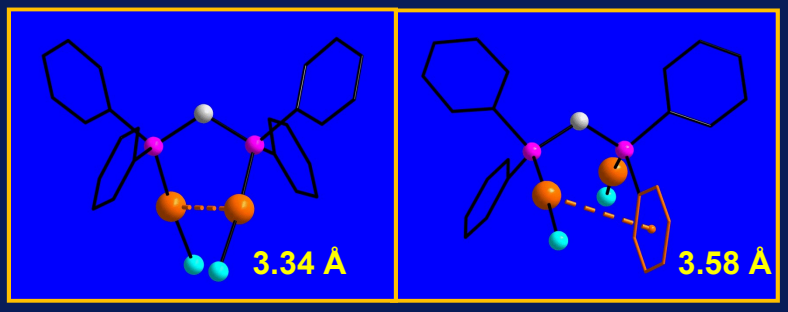
Competition between

i) Au···Au and hydrogen bonding

Comparable in energy to hydrogen bonding

Schmidbaur, *Nature* **413** (2001) 31.

Polymorphs of $(dppm)(AuCl)_2$



Schmidbaur *et al*. *Chem. Ber*. **110** (1977) 1748;
Healy, *Acta Crystallogr. E* **59** (2003) m1112.

Gold Chemistry

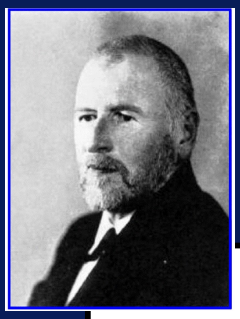
Competition between

i) Au···Au and hydrogen bonding

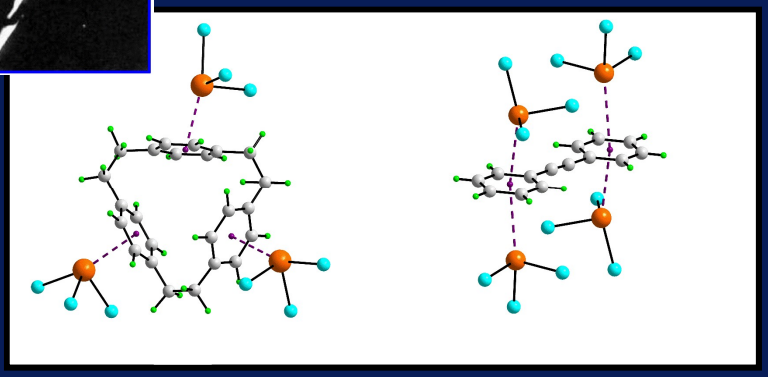
ii) Au···Au and Au···π(arene)

$(HB)^2$: Similar in energy = 5 – 15 kcal/mol

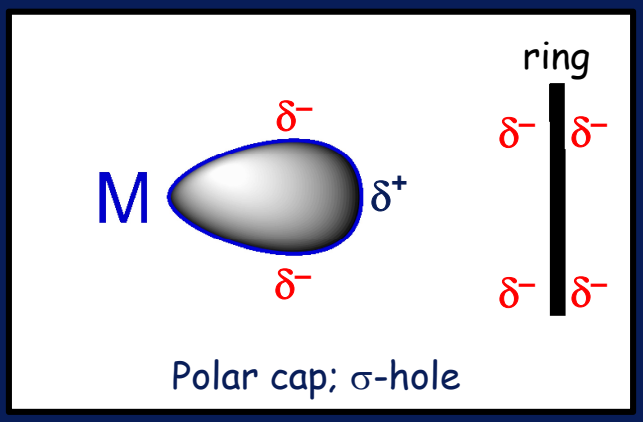
Intermolecular M(lp)···π(arene) interactions



"Menšutkin complexes"

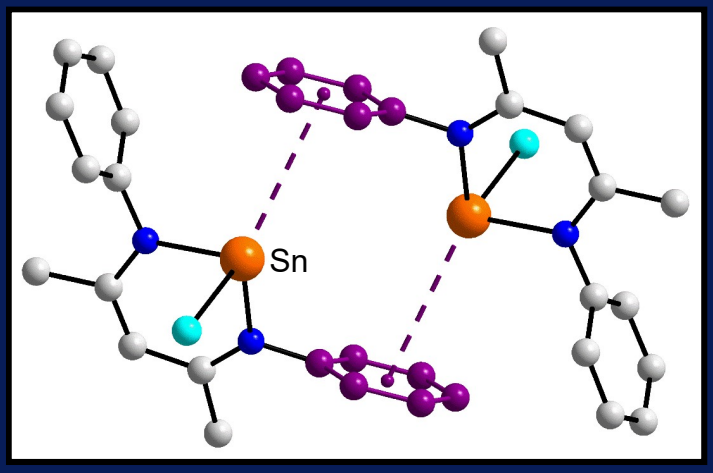


M(lone-pair)···π(arene) interactions?



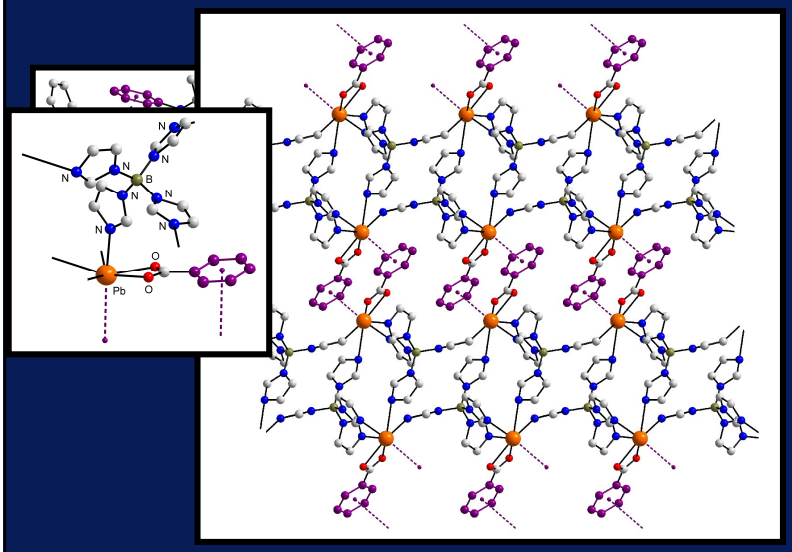
Sigma-hole interactions

Intermolecular M(lp)···π(arene) interactions



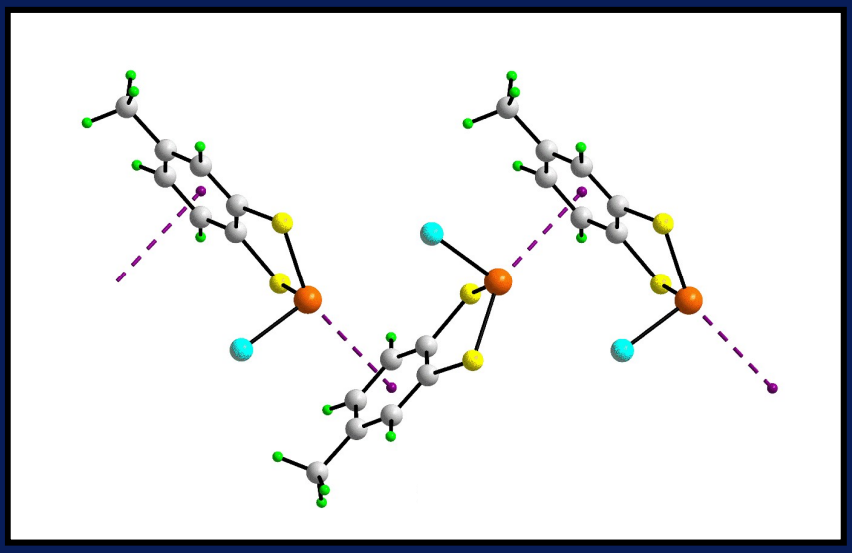
Tin Chemistry: Fundamentals, Frontiers and Applications (2008) Chp. 3

Intermolecular M(lp)···π(arene) interactions



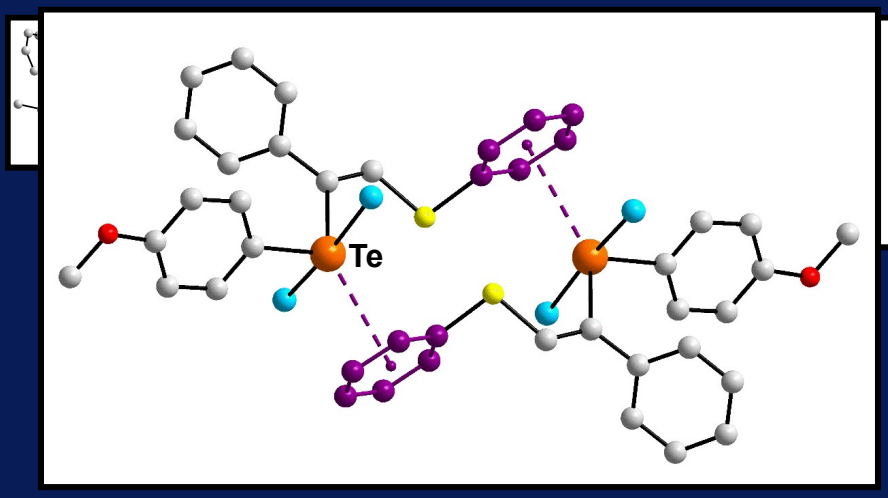
Aust. J. Chem. **63** (2010) 535.

Intermolecular M(lp)···π(arene) interactions



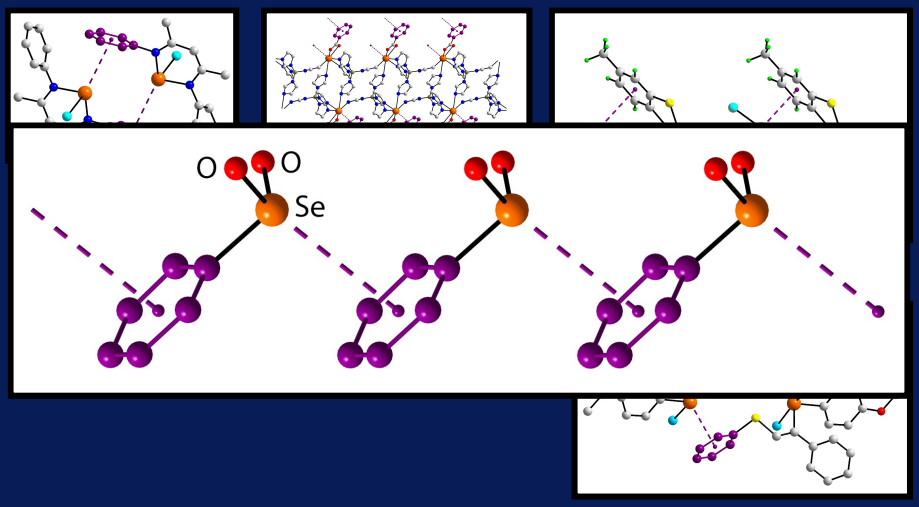
Chem. Commun. **47** (2011) 7608.

Intermolecular M(lp)···π(arene) interactions



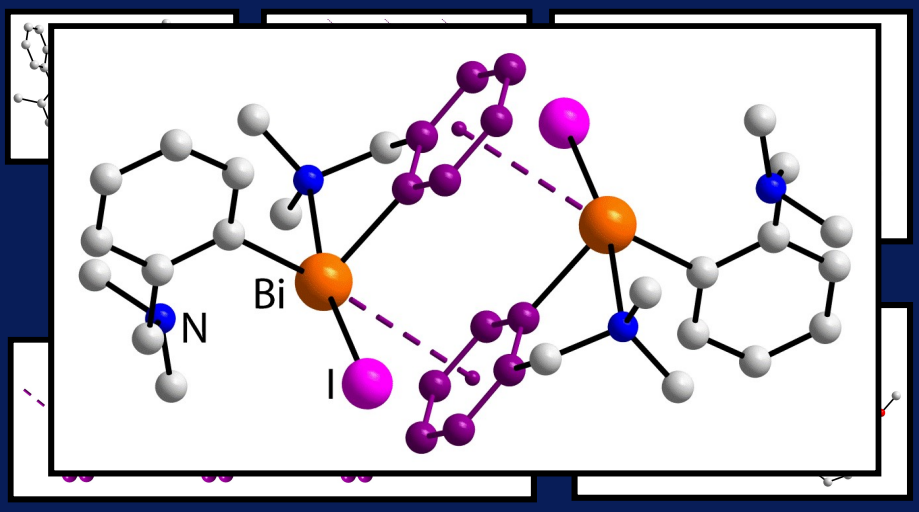
Frontiers in Crystal Engineering II, (2012) Ch. 12.

Intermolecular M(lp)···π(arene) interactions



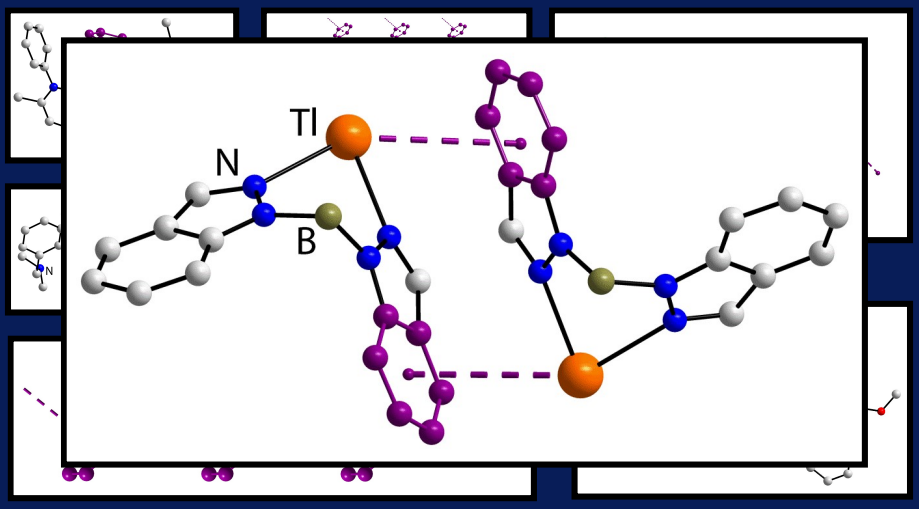
Coord. Chem. Rev. **256** (2012) 412.

Intermolecular M(lp)···π(arene) interactions



Coord. Chem. Rev. **257** (2013) 2863.

Intermolecular M(lp)···π(arene) interactions



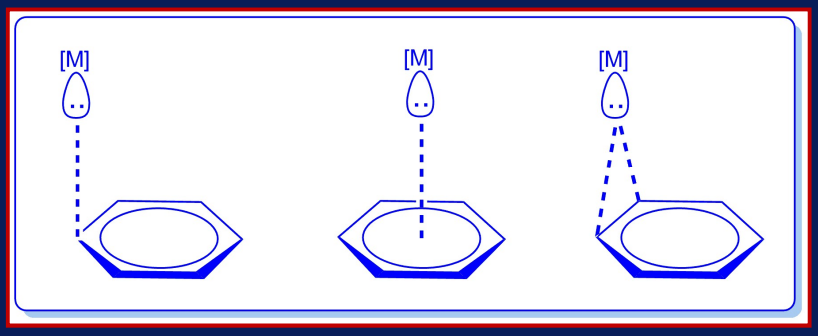
Coord. Chem. Rev. **281** (2014) 50.

Prevalence?

Tl: 14%

Tl(lp)···π(arene) Interactions, CSD Search

Search protocols: $\alpha < 30°$

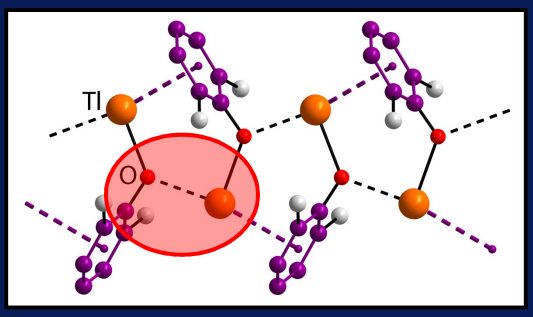


localised

delocalised

semi-localised

Tl(lone pair)...π(arene) Interactions



d = 3.16 Å, α = 4.2°

Excluded, as Tl(lp)...π not operating in isolation

Prevalence?

Tl: 14%

Delocalised/Semi-localised/Localised

Cooperativity

{Au: x7 probability of Au···C}

CrystEngComm **18** (2016) 50; *Mono. Supramol. Chem.* **20** (2017) 6960.

Energy?

ChemComm

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Received 17th December 2015,
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DOI: 10.1039/c5cc10363k

On the nature of the stabilisation of the E···π pnicogen bond in the $SbCl_3$···toluene complex†

Rabindranath Lo,[a] Petr Švec,[b] Zdeňka Růžičková,[b] Aleš Růžička[b] and Pavel Hobza*[ac]

$SbCl_3$ +	C_6H_6	7.7 kcal/mol
	C_6H_5Me	9.6 kcal/mol
	C_6Me_6	15.5 kcal/mol

π(chelate)···π(chelate) interactions

Coordination Chemistry Reviews 345 (2017) 318–341

Contents lists available at ScienceDirect

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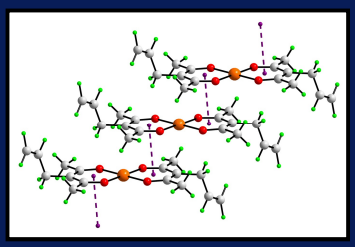
Review

Noncovalent bonding: Stacking interactions of chelate rings of transition metal complexes

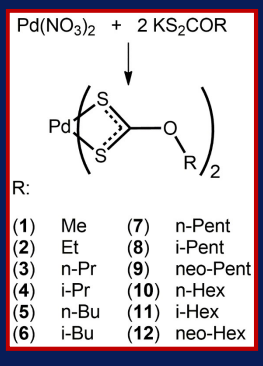
Dušan P. Malenov [a], Goran V. Janjić [b], Vesna B. Medaković [a], Michael B. Hall [c], Snežana D. Zarić [a,d,*]

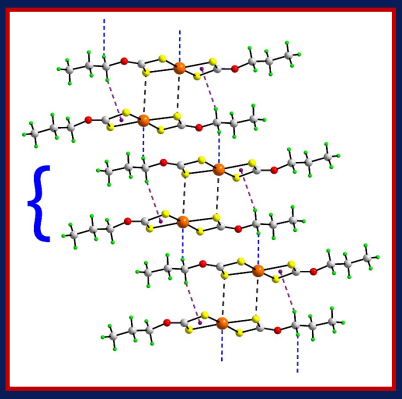


π(chelate)···π(arene) ~ 6 kcal/mol

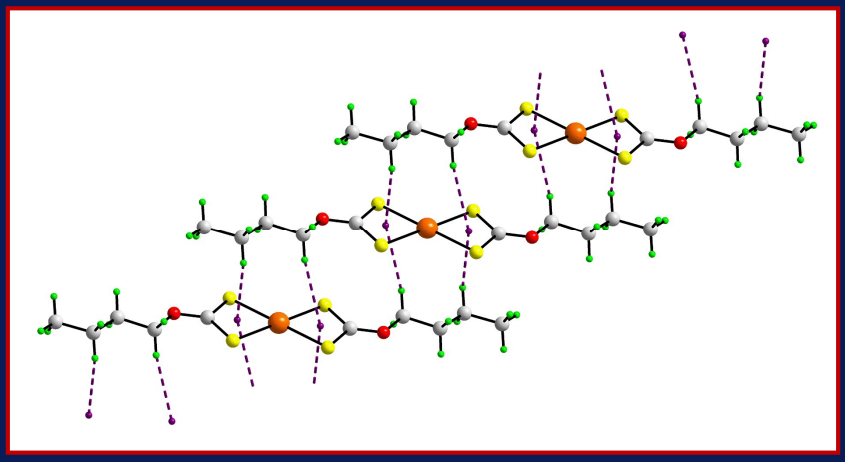
π(chelate)···π(chelate) ~ 9 kcal/mol

C—H···π(chelate) interactions:

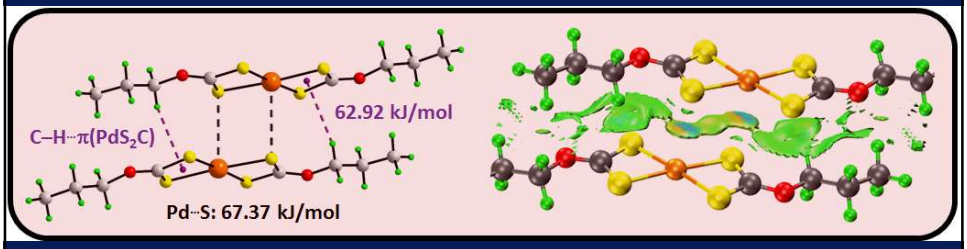




C—H···π(chelate) interactions:



Intermolecular interactions involving chelate rings

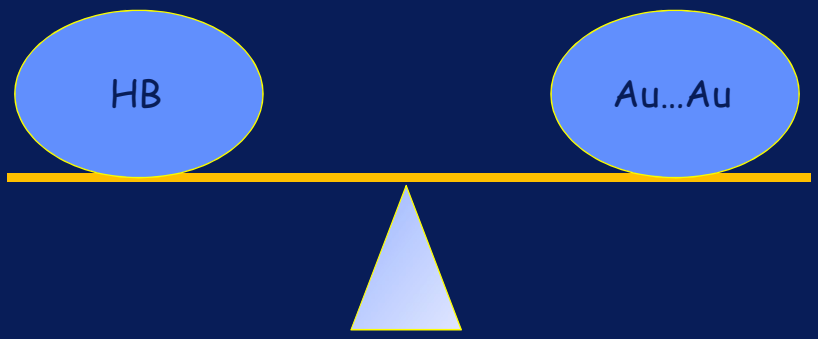


Pd···S	16 kcal/mol
C–H···π(chelate)	15 kcal/mol

Conclusions

More to supramolecular life than $(HB)^2$

"Emerging" interactions are competitive



Coord. Chem. Rev. 345 (2017) 209

Conclusions

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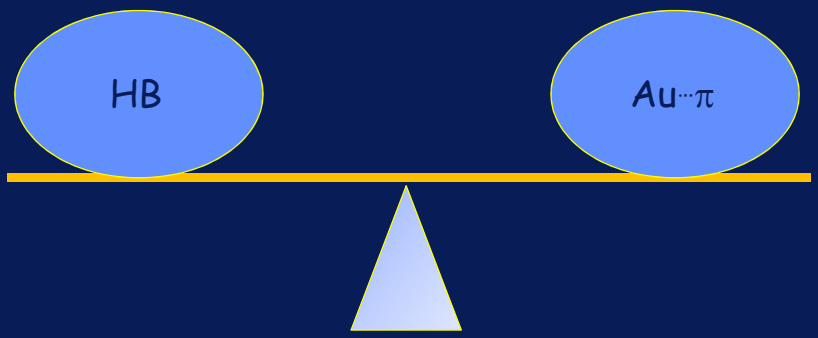

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Conclusions

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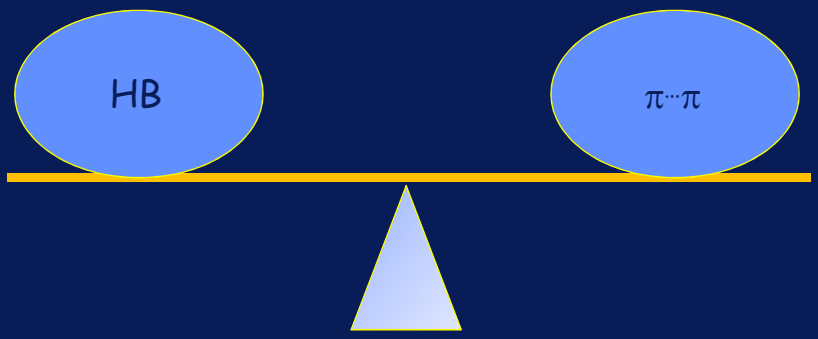

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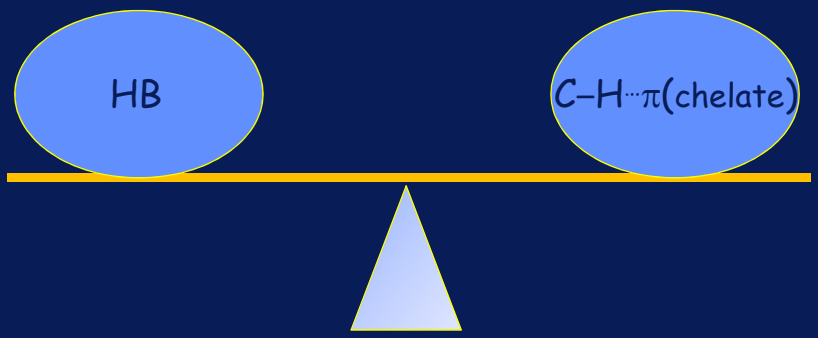

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Conclusions

More to supramolecular life than $(HB)^2$

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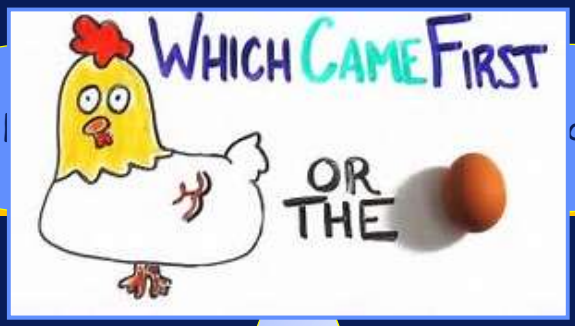
Global molecular packing



chelate)

"Egg Causality Dilemma"

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